Metakaolin clay-derived geopolymer for recycling of waste cathode ray tube glass

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Metakaolin clay (MC)-based geopolymer was used to immobilise waste cathode ray tube (CRT) glass as a method of recycling it into other useful products. Effects of CRT glass on the properties of geopolymer and toxicity status were assessed. A Nigerian MC was replaced with different proportions of ground waste CRT glass (0-20%) and alkali-activated to produce geopolymers. X-ray fluorescence (XRF) was used to characterise CRT and MC. The geopolymers were cured at room temperature for 7, 14, 21 and 28 days. Their setting time, compressive strength, dry density, water absorption and Pb binding abilities were evaluated. Geopolymers were leached using Toxicity Characteristics Leaching Procedure (TCLP). The XRF results revealed the main oxides of MC as SiO$_2$ and Al$_2$O$_3$ and CRT glass as SiO$_2$ and PbO. Setting time of the geopolymers ranged from 1 h (0% CRT) to 2 h (20% CRT). Compressive strength values of the geopolymers increased with percentage composition of CRT glass and curing age. At 28 days, the maximum compressive strength of 36.8±0.4 MPa was obtained for geopolymer that contained 20% CRT glass. Increase addition of CRT glass reduced water absorption and increased the density of the geopolymer. Leachable Pb in the geopolymer extracts was below US EPA TCLP regulatory limit of 5 mg/L. Metakaolin clay geopolymers can be a cost-effective and sustainable binder to recycle CRT into value added products.

Key words: Metakaolin clay geopolymer, immobilisation, cathode ray tube glass, recycling, leachable Pb.

INTRODUCTION

A cathode ray tube (CRT) is a vacuum tube which consists of electron gun(s) and a fluorescent screen and it is used to display images mainly on computers and televisions. It consists of neck glass which houses the electron gun, screen glass which shows the image obtained from electronic signals and a funnel glass that connects the screen and neck. It is usually held in plastic casing. The funnel and neck glass contained large amount of Pb in form of lead oxide (PbO). The screen glass is a non-leaded glass but contains barium oxide. The high amount of Pb in the glass of cathode ray tubes (CRTs) makes them hazardous to the environment when they reach end-of-life.

Waste CRTs are generated mainly from end-of-life computers and televisions. Their generation is usually estimated from first generation spent computers and televisions. In the current technology, computer and television monitors have been substituted with new
devices such as Liquid Crystal Displays (LCDs) and Plasma Display Panel (PDPs). This replacement led to generation of large quantity of outdated computers and televisions in all the countries of the world with consequent production of waste CRTs. Several studies have documented the estimates of waste CRT devices from different countries. Singh et al. (2016) cited that, according to the United Nation University (UNU), the global quantity of waste CRT screen glass generation in 2014 was around 6.3 Mt. with 2.5 Mt in Asia 1.7 Mt in Europe, 1.7 Mt in America, 0.3 Mt in Africa and 0.1 Mt in Oceania. According to a white paper on E-waste Recycling Industry in China, 43.11 million tons of CRT glasses were generated in 2013 (Singh et al., 2017). The authors further documented that in Japan approximately 1.87 million CRT TVS were collected in 2014 and 6.9 Mt of CRTs remain to be recovered from homes and businesses in the U.S. In view of this large amount of the waste CRT glass in circulation, there is need for its sound environmental management.

At the end-of-life, if the monitors are disposed of into the environment indiscriminately or landfilled, the CRT glass can crush, when Pb and other undesirable heavy metals can leach from them (Jang and Townsend, 2003; Inighe et al., 2013) and contaminate, soil, air, groundwater and afterwards food chain. Kim et al. (2005) studied the leaching of heavy metals from waste CRT glass and found that most CRTs exceeded the regulatory threshold of 5 mg/L for Pb and 0.75 mg/L for land disposal restrictions. Since TCLP is meant to simulate the conditions that might likely occur in landfill, their results imply that disposal of waste CRTs on land or in landfill is not the best management option.

Cement has been used as binding material for stabilization of different hazardous wastes. Cases of recycling of waste CRT into concrete using ordinary Portland cement have been reported (Ling and Poon, 2011; 2012; Lairaksa et al., 2013; Sua-iam and Makul, 2013). Sua-iam and Makul (2013) reported that the Pb leaching levels from the cured concrete were within US EPA allowable limits, demonstrating effective Pb encapsulation in the concrete and the glass content of the CRT. However, as cited by Sua-iam and Makul (2013), the use of waste glass as an aggregate in concrete has a slightly negative effect on the workability as well as decreasing the slump, air content, and unit weight of the concrete. Moreover, more water was required to achieve workability. To overcome the weaknesses of the existing management methods, geopolymrization may be a suitable and economic method for management of waste CRT glass.

Geopolymers are solid aluminosilicate materials usually formed by alkali hydroxide or and alkali silicate activation of solid precursors such as commercial pure metakaolin, low purity metakolin clay obtained from local kaolin clay deposits, coal fly ash, and/or metallurgical slag. Geopolymers are alternative greener inorganic binders that can be applied in stabilization of hazardous waste, building and construction as ordinary Portland cement. Geopolymers have been studied as matrices for heavy metals and hazardous waste encapsulation (van Jaarsveld and van Deventer, 1996; Pacheco-Torgal et al., 2007; Ogundiran et al., 2013). They do these by physical encapsulation or the particular metal provides a charge balancing mechanism for the substitution of tetrahedral Si by Al in the geopolymers. Geopolymer technology provides an opportunity to recycle solid and liquid wastes into useful products such as pavement blocks, bricks and concrete in place of disposal which could lead to environmental contamination (Saeed and Zhang, 2012; Kumar and Kumar, 2013). The global initiative towards sustainable technology has engendered studies on the possibility of using wastes materials as part of geopolymer precursors to make the technology sustainable and encourage less use of natural resources like metakaolin clay, continuous mining of which may cause environmental degradation and depletion of natural resources. The glass in the waste may serve as resource materials for production of metakaolin-based geopolymers thereby diminishing the demand for kaolin clay which is a non-renewable resource.

MATERIALS AND METHODS

Material collection and treatment

A Nigerian kaolin clay tagged as Ikere-Ekiti kaolin clay was sourced from natural deposits in Ikere Local Government, Ekiti State. Large amount of the clay sample was dried under sun to reduce its moisture content. The sample was crushed using rolling rod. The crushed clay was air-dried for one week and sieved to 212 µm using Endcott Ltd, London, stainless steel sieve. Waste cathode ray tube was collected from a technician workshop, dismantled and the neck, funnel and panel glasses removed, washed, dried and ground together. This was sieved to 63 µm particle size in accordance with particle size of 75 µm or less to initiate glass pozzolanic reaction (Shao et al., 2000). The kaolin clay was
thermally treated to convert it into amorphous metakaolin clay which is the reactive precursor for geopolymer production, following Ogundiran and Kumar (2015).

### Material characterisation

Chemical composition of the ground waste CRT glass was determined using X-Ray Fluorescence (XRF) Spectrometer (TEFA ORTEC automatic X-ray F) and of the metakaolin clay was adapted as reported previously (Ogundiran and Kumar, 2015).

### Synthesis and characterisation of geopolymer

Sodium hydroxide (NaOH) in form of white flakes and sodium silicate solution with chemical composition of 30.1% SiO$_2$, 9.4% Na$_2$O and 60.5% H$_2$O both of industrial scale were used as the activator. Eight molar (8 M) NaOH solution was prepared by dissolving the appropriate quantity in distilled water and allowed to cool. The Na$_2$SiO$_3$ and NaOH solutions were mixed together in a mixing ratio of (1:1) to form an alkali activator. The alkali activator after preparation was left for about 24 h before use. The ratio of metakaolin clay to ground waste CRT glass were 100:0, 95:5, 90:10, 85:15 and 80:20. The mix proportions are presented in Table 1.

The starting materials were mixed in a mixer for a few but consistent minutes to homogenise the samples. The amount of the activator was added and mixed again with a mixer for a few minutes until a workable paste was obtained. The pastes were cast into plywood cube moulds of 40 mm × 40 mm × 40 mm lined with polyethylene material and vibrated on a table for few minutes for compaction and reduction of entrapped air. Setting time of representative geopolymer pastes were measured as the time between the cast of the geopolymer paste and the time when it solidified completely, preventing the penetration of a needle (Ogundiran et al., 2013). The moulds were covered in polythene bags and allowed to set at room temperature for 3 days. After which the geopolymer samples were demoulded and kept in sealed plastic bags to cure at room temperature. The compressive strength values at 7, 14, 21 and 28 days curing were measured. For each curing time, test was conducted on three geopolymer samples using compression test machine (ELE International, ADR Touch 2000). The maximum force for each geopolymer was divided by the cross-sectional area and the average of the two closest values was taken as the compressive strength. Dry density and water absorption of the geopolymers at 7 and 28 days were measured as reported previously (Ogundiran and Ikotun, 2014).

### Toxicity characteristics leaching procedure test

This test was performed to assess the effectiveness of encapsulation of Pb in the geopolymer networks and the environmental fitness of the CRT-MC geopolymers. Lead (Pb) leaching from the geopolymers after 28 days was assessed using the Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311) as reported previously (Ogundiran et al., 2013). Two (2.0) g of the CRT glass containing geopolymer samples crushed to less than 10 mm and the unstimulated counterparts were extracted with 40 mL of 0.1 M acetic acid solution with initial of pH 2.88 ± 0.05 in capped polyethylene centrifuge tubes. Acetic acid solution at pH = 2.88±0.05 was chosen as extractant since the samples were highly alkaline materials. The extraction vessels were rotated on an end-to-end shaker at 30 rpm for 18 h and filtered to remove suspended solids. The extracts were acidified to pH < 2 prior to instrumental analysis. Quality control included duplicate, blank and blind sample analyses. Atomic absorption spectrophotometer (A-analyst 200) was used to quantify extractable Pb in the extracts.

### RESULTS AND DISCUSSION

#### Material characterisation

From the results of XRF analysis, PbO and SiO$_2$ were found as the main chemical composition of the CRT glass and Na$_2$O, K$_2$O, CaO, BaO and Al$_2$O$_3$ as the minor ones (Table 2). The SiO$_2$ of the CRT glass is amorphous which could participate in geopolymerisation reaction.

#### Water demand and setting time of the geopolymers

Partial replacement of metakaolin clay with waste CRT glass in the synthesis of geopolymer has effect on activator and indirectly water consumption and workability of the geopolymer pastes. One of the disadvantages of metakaolin geopolymer is high water demand which makes its handling difficult in order to achieve sufficient workability. Obviously, CRT glass-MC geopolymers have lower solution-to-binder ratios compared with 100% MC-geopolymers (Table 1). Less solution was required to achieve the same workability with 100% MC-geopolymers. Addition of glass appears to achieve two purposes. The CRT glass contributed reactive silica during geopolymerisation reaction, hence less activator solution as glass addition increased (Table 1). Secondly, the glass probably impacted self-compacting properties on the clay by filling pores among the clay particles, thereby reducing its water absorption ability.

<table>
<thead>
<tr>
<th>% Ratio of MC : CRT glass</th>
<th>Activator/solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>0.82</td>
</tr>
<tr>
<td>95:5</td>
<td>0.78</td>
</tr>
<tr>
<td>90:10</td>
<td>0.73</td>
</tr>
<tr>
<td>85:15</td>
<td>0.69</td>
</tr>
<tr>
<td>80:20</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Table 2. Chemical composition (% wt) of the CRT and metakaolin clay.

<table>
<thead>
<tr>
<th>Oxide (% weight)</th>
<th>CRT</th>
<th>*Calcined clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54.1</td>
<td>55.8</td>
</tr>
<tr>
<td>PbO</td>
<td>24.1</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.72</td>
<td>27.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.32</td>
<td>0.17</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.02</td>
<td>0.23</td>
</tr>
<tr>
<td>CaO</td>
<td>2.45</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.36</td>
<td>1.10</td>
</tr>
<tr>
<td>MgO</td>
<td>1.08</td>
<td>0.06</td>
</tr>
<tr>
<td>BaO</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.16</td>
<td>1.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>SrO</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>LOI</td>
<td>0.21</td>
<td>1.27</td>
</tr>
</tbody>
</table>

*Source: Shao et al., 2000.

Table 3. Setting time of geopolymers with NaOH/Na₂SiO₃ activator and at different CRT additions.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>%CRT</th>
<th>Setting time (h:min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRT-MC geopolymer</td>
<td>0</td>
<td>1:0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1:05</td>
</tr>
<tr>
<td>CRT-MC geopolymer</td>
<td>10</td>
<td>1:20</td>
</tr>
<tr>
<td>CRT-MC geopolymer</td>
<td>15</td>
<td>1:45</td>
</tr>
<tr>
<td>CRT-MC geopolymer</td>
<td>20</td>
<td>2:0</td>
</tr>
</tbody>
</table>

The setting times of CRT-MC geopolymers are presented in Table 3. These were found to range from 1 to 2 h. The setting time was least for the 100% MC-geopolymer and increased as the proportion of CRT glass in the geopolymer increased, showing slow activation of the geopolymer paste. A retarded setting time achieved with addition of waste CRT glass may be an advantage, since it improved geopolymer paste workability for a longer period of time. The fast setting exhibited by the 100% MC-geopolymer may be related to the increase in the dissolution/hydrolysis rate exhibited by the metakaolin clay due to its high Al₂O₃ content, which in effect, increased the initial geopolymer reaction and setting time as stated previously (Ogundiran and Sanjay, 2016). Addition of CRT glass increased the setting time. This implies that waste CRT glass can be used to control initial geopolymerisation reaction: Setting and hardening that accompany synthesis of metakaolin clay geopolymers. Sua-iam and Makul (2013) also reported increase in the setting time of cement concrete due to addition of CRT glass.

Compressive strength of geopolymers

The compressive strength results of the geopolymers made with different proportions of waste CRT glass and metakaolin clay at 7, 14, 21 and 28 days are shown in Table 4. The compressive strength increased with increasing curing period. The increase in compressive strength with curing periods suggests ongoing reactions by the geopolymers with accompanied stronger strength gain. All geopolymers which contained CRT glass exhibited higher compressive strength than 100% MC-geopolymers at all curing ages, and the higher the quantity of the CRT glass, the higher the compressive strength. The CRT glass containing geopolymers displayed better early and later strength gain. Geopolymer with 20% CRT glass replacement exhibited the highest compressive strength at all ages followed by
the geopolymer with 15, 10 and 5% CRT glass respectively. For instance, at 7 days, the compressive strength value of 20% CRT-MC geopolymer increased up to 28 MPa compared with 22 MPa for 100% MC-geopolymer. Similarly, it exhibited compressive strength of about 36 MPa compared with 30 MPa for MC-geopolymers at 28 days. Up to 20% CRT glass addition meets 30 MPa IS 15658 specifications (Kumar and Kumar, 2013) for paving blocks. This implies that the CRT glass-MC geopolymers could be applied as paving materials if they meet environmental standards.

Three reasons among others may be advanced for the variation in the compressive strength of the geopolymers. The effect may be connected with the chemical composition of the glass. The XRF results showed high content of SiO₂ in the composition of CRT glass (Table 2). The silica content of CRT glass is amorphous (Suaiam and Makul, 2013). Amorphous silica is an active component in geopolymerisation reaction. Therefore, the addition of CRT glass possibly improved more participation of Si-O-Si bond in geopolymer network of CRT glass-MC based geopolymers. The Si-O-Si bond has been documented to be stronger than Al-O-Al bonds (Duxson et al., 2005). Reactive Al-O-Al bonds were probably more in the MC-geopolymer and this accounted for lower strength. Secondly, the higher water demand as shown in Table 1, of MC-geopolymers, might have contributed to accelerate geopolymer reaction which resulted in rapid setting, thereby preventing it from forming denser and stronger geopolymer frameworks. This suggests that waste ground CRT glass may be applied to overcome higher water demand of MC-based geopolymers. Another factor that may be considered to be responsible for the increase in strength was the presence of Pb in the geopolymer network. The Pb in the network might have acted as a network former, a network modifier, or a charge supplier (Ogundiran et al., 2013).

### Water absorption capacity of geopolymers

Water absorption is useful to assess the capability of construction materials to absorb water under specified conditions and it depends on the microstructure and porosity of the materials. The more compact and less porous the structure, the less the amount of water absorbs by the construction materials. It is an important factor considered in the determination of durability of building materials. It is usually done to determine the resistivity of geopolymers to water. Water absorption can also be an indicator of the degree of geopolymerisation reaction (Saeed and Zhang, 2012). The results of the 7 and 28 days water absorption of the geopolymers are shown in Figure 1. The water absorption capacity ranged between 0.38 (20% CRT) and 1.87 (5% CRT). This range was far less than 7% water absorption specification for paving blocks (Kumar and Kumar, 2013), which means in terms of water absorption CRT-MC geopolymers can be applied as paving materials. Increase in CRT glass addition decreased the amount of water absorbed by the geopolymers. Geopolymer samples consisting of 100% metakaolin clay showed the highest percentage of water absorption capacity while geopolymers with higher content of CRT glass had the lowest. This demonstrates that waste CRT glass has potential to make metakaolin clay geopolymers to be less porous and improve their ability to limit water infiltration.

### Dry density of the geopolymers

The results of dry density of the geopolymers after 28 days curing are depicted in Figure 2. The geopolymers dry density is in the range of 1830 to 2020 kg/m³. Increase in the amount of CRT glass increased density. This is contrary to what was reported previously, when ground waste window glass addition decreased the density of metakaolin clay geopolymers (Ogundiran and Winjobi, 2015). The difference might be due to the presence of Pb in the CRT glass which increased the bulk density of the geopolymers. Lead is a heavy element with atomic weight of 207.2 g/mol.

### Toxicity characteristic leaching procedure

The results of Pb leaching for the unstabilised starting materials and the geopolymer counterparts as determined by TCLP are presented in Figure 3. This test was performed to determine the effectiveness of geopolymer networks in binding Pb in waste CRT glass as an alternative method to manage the waste and
secondly to assess environmental fitness of CRT glass-MC geopolymers for potential uses. The leachable Pb ranged from 0.51 to 48.8 mg/L and from 0.27 to 4.28 mg/L in the unstabilised solids and geopolymers respectively. Increase addition of CRT glass increased leachable Pb from the geopolymers. The amount of leachable Pb in the unstabilised solid extracts of mixture of CRT glass and MC were above the US EPA TCLP hazardous limit of 5 mg/L and below the limit in all the geopolymer extracts. The results indicated that the levels of leachable Pb of the geopolymers were substantially reduced compared with their unstabilised counterparts due to the immobilisation of the Pb in the geopolymers. A solid material is considered toxic if the TCLP limit is exceeded. This implies that the MC-geopolymers possessed ability to render spent CRT glass non-toxic. Up to 99.4% Pb was immobilised in 15% CRT glass-MC geopolymer showing the highest binding capacity. Up to 15% CRT addition, the leachable Pb (0.23 mg/L) was much less than the land disposal limit of 0.75 mg/L for CRT (Kim et al., 2005.). This implies that CRT-metakaolin geopolymers up to 15% CRT addition can be applied as construction materials such as paving materials without environmental adverse effects. About 91.2% of Pb in 20% CRT glass-MC geopolymer was immobilised, showing decline in immobilisation power with increase in CRT glass. This observation may imply oversaturation of geopolymer network with Pb. These results established...
that it is possible to use waste CRT glass and metakaolin clay as precursors for synthesis of geopolymers. Also, metakaolin clay geopolymers can effectively immobilise CRT glass, thereby preventing leaching of Pb.

Conclusion

Immobilisation of waste cathode ray tubes (CRTs) glass using metakaolin clay geopolymer was evaluated as an alternative, environment friendly and cost effective method of managing waste cathode ray tube glass. Selected physical, mechanical, durability and environmental properties of waste cathode ray tube glass-metakolin clay geopolymers were assessed. Based on the results the following conclusions were drawn. The geopolymers with waste cathode ray tube glass have better workability, higher setting time, early and late compressive strength gain, water resistance and dry density. The leachability of Pb up to 20% metakaolin clay replacement did not exceed regulatory limit rendering the waste cathode ray tube glass in the geopolymer non-toxic. At 28 days, geopolymers containing 20% CRT glass exhibited highest compressive strength, had leachable Pb below 5 mg/L USEPA limit with water absorption of 0.38%, ascertaining environmental safety and durability potentials of the mixed geopolymers. Therefore, it is feasible to use waste CRT glass in combination with metakaolin clay to produce inorganic binders that may be applied as construction materials. Further studies are required to confirm the reactions involved in the geopolymerisation of CRT glass and validate the reported results.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES


